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INFRARED SPECTRA OF COMPOUNDS OF
UREA WITH ACIDS

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INFRARED SPECTRA OF COMPOUNDS OF
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by

V. A. Veremzhanov, et al

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13. ABSTRACT

IR-spectra have been studied of crystals of urea nitrate, urea phosphate, urea sulphate, diurea sulphate, diurea chloride, urea oxalate, diurea oxalate. It has been established that in the nitrate, phosphate, and sulfates of urea, hydrogen bonding follows the scheme N...H, and in the chloride and oxalates of urea, follows the scheme C=O...H.

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INFRARED SPECTRA OF COMPOUNDS OF
UREA WITH ACIDS

The purpose of the present work was to clarify the question of the sites of bonds in coordination compounds formed by urea with certain acids¹. IR-spectra of the following compounds were obtained: $\text{CO}(\text{NH}_2)_2 \cdot \text{HNO}_3$, $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_3\text{PO}_4$, $2\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{SO}_4$, $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{SO}_4$, $2\text{CO}(\text{NH}_2)_2 \cdot \text{HCl}$, $2\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{C}_2\text{O}_4$, $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{C}_2\text{O}_4$. All of these preparations were synthesized by means of their release from lines of crystallization in ternary water urea-acid systems /1,2/. Correspondingly soluble compounds, such as $\text{CO}(\text{NH}_2)_2 \cdot \text{HNO}_3$, $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_3\text{PO}_4$, $2\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{SO}_4$, $2\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{C}_2\text{O}_4$, were recrystallized from water.

Spectra were recorded on a UR-20 spectrophotometer. It is known that in complexes formed by urea with inorganic compounds, coordination bonds may be formed both by atoms of oxygen, and by atoms of nitrogen /3,4/. In our case the disproportionation of electron density in the urea molecule occurs under the influence of a proton of oxygen, capable of accepting an electron pair.

¹The present work was carried out in the laboratory of physical methods of research of the Institute of Chemical Science of the Academy of Sciences of the Kazakh SSR under the direction of O.V. Agashkin, to whom the authors express their thanks.

If such a bond was achieved between an acceptor and nitrogen as a result of an available pair of electrons on the nitrogen, the frequency of CN bonds should decrease. At the same time, as a result of the partial relief of π -electrons of the CO bond from union with π -electrons of nitrogen, the frequency of valence vibration of this bond should increase in comparison to the frequency in pure crystalline urea; therefore, the CO bond should become more stable.

If this bond in the coordination compounds exists through an atom of oxygen, the results will be reversed. The frequency of the valence vibration of CO must decrease since the π -electrons of oxygen are divided between oxygen and the acceptor. The CN bond becomes more stable.

In the table wave numbers are presented for absorption maxima (in cm^{-1}) in IR-spectra of absorption of urea and its compounds with acids (See figure). The spectra was studied in more detail in the region of frequencies 700-1800 and 2800-3500 cm^{-1} , where all the basic bands of absorption of CN, CO, and NH bonds of urea are located.

Wave Numbers of Absorption Maxima (in cm^{-1}),
Found in IR-spectra of Absorption
Of Urea and its Compounds of Acids.

| $\text{CO}(\text{NH}_2)_2$ | $\text{CO}(\text{NH}_2)_2 \cdot \text{HNO}_3$ | $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_3\text{PO}_4$ | $2\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{SO}_4$ | $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{SO}_4$ | $2\text{CO}(\text{NH}_2)_2 \cdot \text{HCl}$ | $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{C}_2\text{O}_4$ | $2\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{C}_2\text{O}_4$ |
|--|---|--|---|--|--|---|--|
| $\nu(\text{NH})$ | 3443 3340 3210 | 3443 3340 3210 | 3455 3340 3210 | | | 3443 3340 3243 | 3443 3340 3243 |
| $\nu_s(\text{CO})_2(\text{NH}_2)$ | 1665 | 1665 | 1665 | 1665 | 1665 | 1645 | 1675 |
| $\nu_s(\text{CO})_2(\text{NH}_2)$ | 1620 | 1710 | 1630 | 1713 1578 | 1713 1565 | 1630 | 1640 |
| $\nu_{as}(\text{CN})$ | 1452 | 1390 | 1387 | 1388 1330 1300 | 1388 | 1470 | 1525 1320 |
| $\delta_s(\text{NH}_2)_{\text{MANTH}}$ | 1170 | | 1240 | 1170 | 1140 | 1155 | 1240 |
| $\nu_s(\text{CN})$ | 1075 | 1060 | 1082 | 1088 | | 1110 | 1157 |

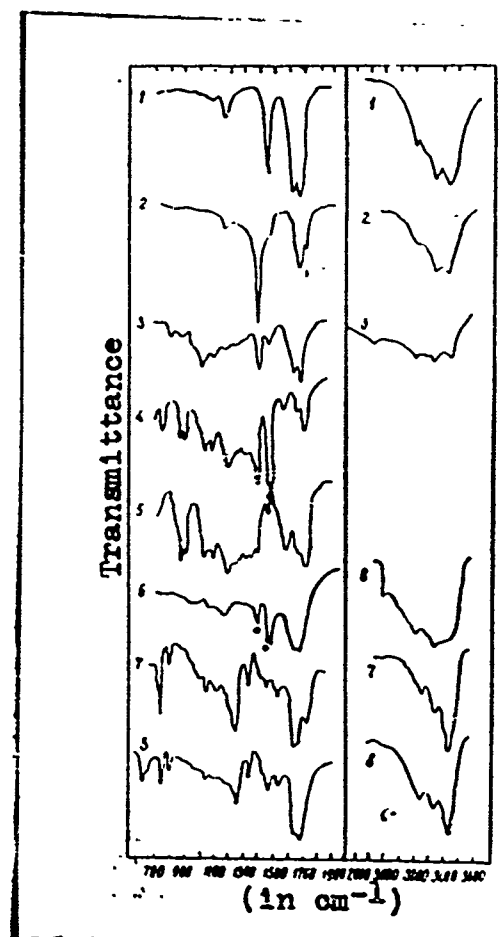
In our compounds of urea with mineral acids one should point out the absence of two types of bands, corresponding to valence vibration of free and coordinated NH_2 groups of molecules of urea in contrast to that observed in spectra of complex compounds of Pt^{++} and Pd^{++} with urea /3/. The width and position of the absorption band in this region is almost indistinguishable from the absorption band of the valence vibration of NH of crystal and urea. Therefore, we did not have to work with data in the region $2800\text{--}3500\text{ cm}^{-1}$.

The band at a frequency of 1665 cm^{-1} in the urea spectrum, which is related to the deformation vibration of NH_2 , appeared in all spectra of urea compounds with acid almost without change. Only in the case of $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{C}_2\text{O}_4$ it shifts ($\Delta=20\text{ cm}^{-1}$) to the side of lower frequency.

Scans are presented below for spectra of: the compounds: $\text{CO}(\text{NH}_2)_2 \cdot \text{HNO}_3$, the nitric acid of urea, urea nitrate. Analysis of the spectra of nitric acid of urea and comparison of it with a spectrum for pure urea indicates the existence of bonds between nitrogens of one of the amino groups. Actually, the absorption band with frequency 1452 cm^{-1} , pertaining to the valence vibration of the bonds in pure urea, shifted to the side of lower frequencies to 1390 cm^{-1} in the spectrum of the compound, by merging with the band of NO_3^- -anion. The shift in frequency of 62 cm^{-1} indicates a reduction in double bonding; on the other hand, the shortness of the CO bonds noticeably increase, which demonstrates the shift in the band with 1620 cm^{-1} of the valence vibration of CO in the region of 1710 cm^{-1} .

In $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_3\text{PO}_4$, the phosphoric acid of urea, urea phosphate, the bond between the molecule of urea and phosphoric acid also exist through one of the nitrogen atoms of urea. The band at about 1387 cm^{-1} in the spectrum of the compound pertains to the valence vibration of the CN -bond; the shift towards lower frequency region is on the same order as in the spectrum of urea nitrate. However, the band characterizing the valence vibration of the carbonyl group, undergoes a slight change; $\Delta=10\text{ cm}^{-1}$.

By x-ray structural research of urea phosphate /5/ it was also shown that in a perturbed molecule the CN distance is somewhat increased, and the CO distance somewhat decreased.



Spectra of Compounds of Urea with Acids.

1- $(\text{NH}_2)_2\text{CO}$, 2- $(\text{NH}_2)_2\text{CO} \cdot \text{HNO}_3$, 3- $(\text{NH}_2)_2\text{CO} \cdot \text{H}_3\text{PO}_4$,
 4- $(\text{NH}_2)_2\text{CO} \cdot \text{H}_2\text{SO}_4$, 5- $2(\text{NH}_2)_2\text{CO} \cdot \text{H}_2\text{SO}_4$, 6- $2(\text{NH}_2)_2\text{CO} \cdot$
 $\cdot \text{HCl}$, 7- $(\text{NH}_2)_2\text{CO} \cdot \text{H}_2\text{C}_2\text{O}_4$, 8- $2(\text{NH}_2)_2\text{CO} \cdot \text{H}_2\text{C}_2\text{O}_4$.

* - Bands of mineral oil.

$\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{SO}_4$ is the sulfuric acid of urea, urea (mono)² sulfate.

$2\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{SO}_4$ is sulfuric acid diurea, diurea sulphate.

As a result of strong moisture absorbing properties, the spectra of both sulphates were taken in mineral oil. But clear graphs in the 3μ region were not obtained. Therefore, they are not presented.

Absorption bands, corresponding to the basic valence vibrations of CO and CN-bonds in the spectra of both complexes, are at 1713 cm^{-1} and 1388 cm^{-1} . The band at 1380 cm^{-1} of mineral oil broadens as a result of the absorption band caused by the valence vibration of the CN bond of urea sulphates. The CO line becomes more intensive and crosses the NH_2 line of deformation vibration at 1665 cm^{-1} . An increase in the value of the frequency 1620 cm^{-1} and a decrease in the frequency 1452 cm^{-1} , corresponding to unperturbed urea, indicates the formation of nitrogen bonds. The shifts in bands are rather great - 93 and 64 cm^{-1} .

$2\text{CO}(\text{NH}_2)_2 \cdot \text{HCl}$, hydrochloric acid diurea, diurea chloride. Spectra were recorded in mineral oil. Diurea chloride occupies different positions depending on the type of bond. This is explained by the characteristic of this compound, where two molecules of urea are bonded with one molecule of a monobasic acid, although, as is known, urea is excessible in compounds of many acids as a monoacid base. This anomaly in diurea chloride may have explained its capacity for self association in construction of crystal lattices, and also in solutions of weakly polar solvents. However, IR-spectra do not permit the termination of absolute displacement in the frequencies of various groups of urea due to association. Diurea chloride has not been isolated from aqueous solutions; it is obtained from a melt of urea by bubbling hydrogen chloride. In our opinion, self association of molecules of urea enters into the compound in the form of dimers. The behavior of frequencies characterizing bonds in the spectrum of this compound, make it possible to assume the formation of bonds to the oxygen of the carbonyl group, since it is displaced towards the higher frequency region with a maximum at about 1470 cm^{-1} . It is extremely difficult to determine the position of the frequency of the CO-bond, since it is taken into consideration in the wide band $1620\text{-}1660 \text{ cm}^{-1}$ together with

the band of deformation vibration of the NH_2 group.

$\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{C}_2\text{O}_4$, oxalic acid urea, urea (mono) oxalate.

$2\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{C}_2\text{O}_4$, oxalic acid diurea, diurea oxalate.

In the set of frequencies characterizing urea oxalate, only the absorption band of the CN bond is of special interest, since its precise displacement permits one to reveal the character in the compounds formed between urea and oxalic acid. While in pure urea the valence anti-symmetrical vibrations of the CN-bond corresponds to a frequency of 1452 cm^{-1} , in the spectra of both compounds this shifts to the region of 1525 cm^{-1} , which is the result of strengthening of this bond. This is possible only in the case of formation of a bond of the type $\text{C}=\text{O} \dots \text{H}$. The oxygen of the carbonyl group is available as an electron donor during formation of the hydrogen bond in compounds with oxalic acid.

In IR-spectra of oxalate compounds of urea, the participation of OH group oxygen has not been established. Apparently, it has a low intensity and is overlapped by other more decisive bands.

Conclusions

1. IR-spectra have been studied of crystals of urea nitrate, urea phosphate, urea sulphate, diurea sulphate, diurea chloride, urea oxalate, and diurea oxalate.
2. It has been established that in the nitrate, phosphate, and sulphates of urea the hydrogen bond appears according to the scheme $\text{N} \dots \text{H}$, and in the chloride and oxalates of urea - according to the scheme $\text{C}=\text{O} \dots \text{H}$.

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